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Full *S* matrix calculation via a single real-symmetric Lanczos recursion: The Lanczos artificial boundary inhomogeneity method

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We present an efficient and robust method for the calculation of all *S* matrix elements (elastic, inelastic, and reactive) over an arbitrary energy range from a single real-symmetric Lanczos recursion. Our new method transforms the fundamental equations associated with Light's artificial boundary inhomogeneity approach [J. Chem. Phys. **102**, 3262 (1995)] from the *primary representation* (original grid or basis representation of the Hamiltonian or its function) into a single *tridiagonal Lanczos representation*, thereby affording an iterative version of the original algorithm with greatly superior scaling properties. The method has important advantages over existing iterative quantum dynamical scattering methods: (a) the numerically intensive matrix propagation proceeds with real symmetric algebra, which is inherently more stable than its complex symmetric counterpart; (b) no complex absorbing potential or real damping operator is required, saving much of the exterior grid space which is commonly needed to support these operators and also removing the associated parameter dependence. Test calculations are presented for the collinear $H+H_2$ reaction, revealing excellent performance characteristics. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1640614]

The *S* matrix is the most fundamental quantity in chemical reaction dynamics calculations. Time-dependent (TD)[1] and time-independent (TI)[2] wave packet methods have emerged as powerful tools for calculating such important quantities. These methods can provide one column of the full scattering matrix for arbitrary energies from a single propagation. In recent years attempts have been made to develop generalized iterative quantum dynamical methods which would facilitate the calculation of the full *S* matrix from a single matrix recursion—the real damped Chebyshev recursion and the complex Lanczos recursion have been utilized to date.[3] While very attractive in principle, these methods have not become as popular as TD or TI wave packet methods due to their lack of numerical stability, which has prevented successful implementation for more challenging molecular systems.

In this Letter we present a new single-subspace iterative quantum dynamical algorithm which has a number of advantages over the earlier methods. Based on a spectral implementation of the Lanczos absorbing boundary inhomogeneity (LABI) method,[4,5] our approach utilizes a real-symmetric Lanczos recursion, well known to be significantly more stable than its complex-symmetric counterpart.[6,7] Furthermore, in contrast to the real Chebychev recursion scattering methods,[8] it does not require the use of a real damping operator (RDO) to enforce dissipative boundary conditions. The new spectral LABI method therefore avoids the need to explicitly incorporate into the primary basis the large slice of exterior grid space that is commonly needed to support either a complex absorbing potential (CAP) or a RDO. It also thereby avoids the implicit parameter dependence associated with the definition of the CAP or the RDO. For simple scattering problems this parameter dependence is benign—in the sense of stabilization theory the results become independent of the parameters in the region of convergence. However, for more challenging molecular problems such as scattering at near-threshold energies or resonance-dominated scattering through deep-well intermediates, the issue of parameter dependence associated with imperfect imposition of boundary conditions is much more difficult to satisfactorily resolve using the existing CAP or RDO mechanisms.

The central aspect of the LABI approach is to transform the primary representation of the modified Schrödinger equation[9]

$$(E-H)|\Psi_j\rangle=|B_j\rangle, \tag{1}$$

into a tridiagonal Lanczos representation through the standard three-term Lanczos recursion,[10]

$$\beta_{k+1}\nu_{k+1}=\hat{H}\nu_k-\alpha_k\nu_k-\beta_k\nu_{k-1}. \tag{2}$$

Here the Lanczos vectors $\{\nu_1,\nu_2,\ldots\ldots,\nu_M\}$ tridiagonalize the Hamiltonian matrix $\hat{H}$. The $M\times M$ tridiagonal representation of the Hamiltonian, $\mathbf{T}_M$, has diagonal elements $\alpha_k=(\nu_k|\hat{H}|\nu_k)$ and subdiagonal elements $\beta_k=(\nu_{k-1}|\hat{H}|\nu_k)$. Within the Lanczos representation, the subspace equations take the following form:

$$(E-\mathbf{T}_M)|\phi_j\rangle=|a_j\rangle. \tag{3}$$

In Eq. (3), $|a_j\rangle$ will be the subspace representation of the inhomogeneity $|B_j\rangle$ and $|\phi_j\rangle$ is that of the wave function $|\Psi_j\rangle$. In Eq. (1), the localized boundary inhomogeneity $|B_j\rangle$

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is nonzero only in a narrow boundary region external to the interaction region. Within the interaction region, the solution $|\Psi_j\rangle$ is therefore a regular (noncausal) solution of the standard homogeneous time-independent Schrödinger equation. Our purpose is to obtain a linearly independent set of such solutions $|\Psi_j\rangle$, which is then used as basis to expand the casual scattering waves and subsequently extract the scattering information. The linear independence of the wave functions $|\Psi_j\rangle$ is ensured by choosing linearly independent inhomogeneities $|B_j\rangle$.

The procedure for computing the correct linear combinations of the noncausal wave functions $|\Psi_j\rangle$ which generates the true scattering waves follows the ABI analysis introduced by Jang and Light.[9] Utilizing this approach, a relatively small-sized linear system

$$\mathbf{\Psi}\cdot\mathbf{C}=\mathbf{I}-\mathbf{O}\cdot\mathbf{S} \tag{4}$$

is obtained for a given scattering energy E by first writing out the equation which defines the correct asymptotic boundary conditions for the scattering waves and then projecting from the left with the set of asymptotically open channel eigenfunctions $\langle\varepsilon|$ at two analysis points $\langle R^{\infty}|$ along the asymptotic (reactant and product) scattering coordinates (here $\langle Q_i|=\langle R^{\infty}\varepsilon|$). This is one of two projection strategies proposed by Jang and Light, and is the same approach as adopted in our earlier LABI studies.[4,5] With this projection scheme, the matrices **I** and **O** in Eq. (4) are associated with the incoming and outgoing plane waves in the open scattering channels, and can be analytically calculated in the primary basis. The key quantity which demands most of the computational effort to evaluate is the projection matrix Ψ with elements $\Psi_{ij}=\langle Q_i|\Psi_j\rangle$. Equation (4) is solved using standard LU decomposition[11] to calculate the $\boldsymbol{S}$ matrix and coefficient matrix $\boldsymbol{c}$.

In our previous investigations,[4] we have proposed to solve Eq. (1) over arbitrary energies with a series of Lanczos recursions, each recursion seeded by a different inhomogeneity $|B_j\rangle$. Such a method is a multi-propagation method and one can get all $\boldsymbol{S}$ matrix elements only after all the propagations are completed. In this study, we implement a spectral Lanczos representation of the noncausal Green operator to calculate the Ψ matrix

$$\Psi_{ij}=\sum_{n=1}^{n_{\max}}\frac{\langle Q_i|\xi_n\rangle\langle\xi_n|B_j\rangle}{E-E_n} \tag{5a}$$

$$=\sum_{n=1}^{n_{\max}}\frac{\Sigma_{k=1}^{M^{(n)}}\eta_k(E_n)\langle Q_i|\nu_k\rangle\Sigma_{k=1}^{M^{(n)}}\eta_k(E_n)\langle\nu_k|B_j\rangle}{E-E_n}. \tag{5b}$$

In Eq. (5a) we use $|\xi_n\rangle$ to express the eigenvectors of the real Hamiltonian on the full grid (including the boundary region) in order to distinguish it from the wave function $|\Psi_j\rangle$ from Eq. (1). E_n is the corresponding eigenvalue, and $n_{\max}$ is the number of the eigenpairs of **H**. We employ a Lanczos homogeneous filter diagonalization method[12] to calculate all the eigenvalues E_n. Spurious eigenvalues or copies of true eigenvalues are removed by examining the subspace error norms. The eigenvalues are compared with those from standard Cullum and Willoughby (CW) procedures[6] and the relative errors are within 10^{-7} cm^{-1} or less for all the eigenvalues. The subspace eigenvector $|\eta(E_n)\rangle$ can be efficiently generated by the three-term backward recursion[12] once the eigenvalue is known. There does, however, exist a critical iteration depth $M^{(n)}$ for each eigenvalue n, which is the number of Lanczos iterations needed to accurately converge the eigenpair. We determine $M^{(n)}$ by repeatedly computing the subspace eigenvector for different iteration depths and monitoring the last element $\eta_{M^{(n)}}(E_n)$ of the subspace eigenvector, which is well-known as the subspace estimate to the true error norm.[6] When $\eta_{M^{(n)}}(E_n)$ reaches 10^{-7}, the eigenvector is well-converged[6] and the corresponding iteration depth is taken as $M^{(n)}$.

We stress that our calculations have two separated parts: The first part involves generating the Lanczos subspace from a random seed vector and accumulating (a) the tridiagonal matrix elements and (b) the overlap integrals $\langle Q_i|\nu_k\rangle$ and $\langle\nu_k|B_j\rangle$ of Eq. (5b). For completeness, note that $\langle\nu_k|B_j\rangle$ is actually the kth element of $|a_j\rangle$—the subspace representation of the inhomogeneity—in Eq. 3. This is the most time consuming part of the entire operation. Subsequent subspace calculations of the eigenpairs in Eq. (5b), as well as the ABI analysis to extract all $\boldsymbol{S}$ matrix elements over an arbitrary scattering energy range, can be carried out separately after the main part of the calculations. Though conceptionally more complex, this latter stage takes much less cpu time.

In the following we present the results for the collinear $H+H_2$ reaction using the present spectral (single-subspace) LABI method. The details of the representation of the Hamiltonian and the inhomogeneities B_j are similar to previous calculations[4] and are not given here, and the Liu–Siegbahn–Truhlar–Horowitz (LSTH) potential energy surface[13] was employed in all the calculations. All **S** matrix elements (including reactive and nonreactive) have been calculated for

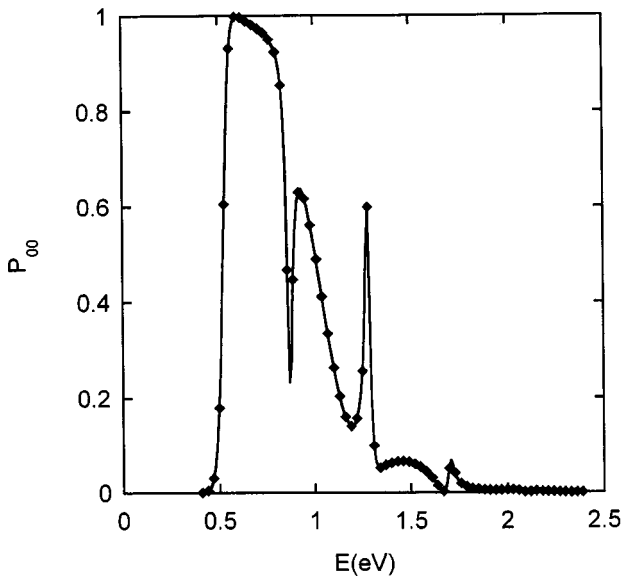

FIG. 1. The state-to-state reactive probabilities $P_{\nu\nu'}$ for the collinear $H+H_2(\nu=0)\rightarrow H_2(\nu'=0)+H$ exchange reaction. The solid line represents the results from real single subspace ABI method, whereas the diamonds represent the results from direct diagonalization in the primary representation.

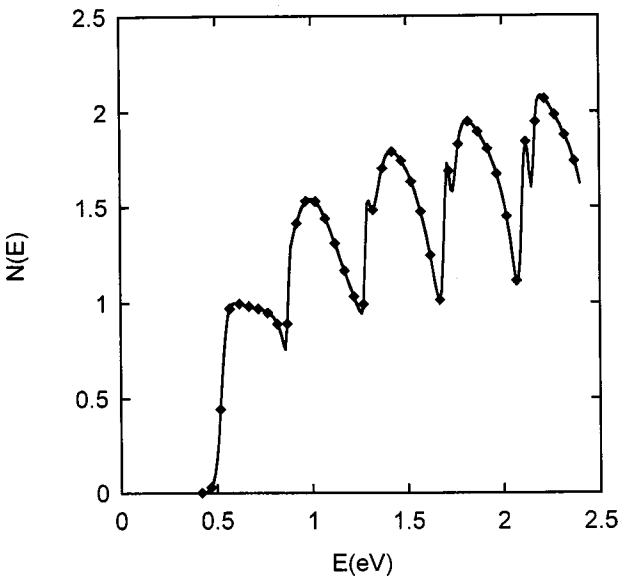

FIG. 2. The cumulative reaction probabilities $N(E)$ for the collinear $H+H_2 \rightarrow H_2+H$ exchange reaction. Other symbols are the same as in Fig. 1.

energies from 0.4 to 2.4 eV, and in Fig. 1 we select one state-to-state reaction probability profile, $P_{00}(E)$, to present. In this figure, the solid line represents the results from this single subspace method, whereas the diamonds represent the results from direct diagonalization in the primary representation for comparison [see Eq. (5a) for details]. Here direct diagonalization consumes much more cpu time and also requires substantial large memory. Inspection of the figure indicates that the agreement of the two methods is quite satisfactory. These results are also in excellent agreement with previous calculations (see, e.g., Ref. 14). After acquiring all the state-to-state reaction probabilities, it is straightforward to calculate the total reaction probabilities from a given reactant state or the cumulative reaction probabilities. In Fig. 2 we plot the cumulative probabilities from the two methods in the energy range from 0.4 to 2.4 eV for comparison. At all energies the agreement of the two methods is quite satisfactory. We note that not all the eigenpairs of the primary (real) Hamiltonian need be converged in order to obtain the converged state-to-state reaction probabilities in this energy range, i.e., 13000 Lanczos iterations can converge all the eigenvectors, but 8000 iterations are needed to converge all the probabilities in this energy range. Compared with previous multi-propagation Lanczos ABI method[4] for $H+H_2$ reaction (4000 iterations for each propagation and five propagations needed), a minimal doubling of efficiency can be achieved using the present spectral LABI approach. This efficiency will be further improved for other systems without symmetry since the necessary number of boundary inhomogeneities is halved in the present symmetrical application.

In conclusion, we have implemented a very efficient spectral Lanczos ABI method to calculate all $\boldsymbol{S}$ matrix elements from a single recursion. Similar to the real Chebyshev wave packet method, this Lanczos algorithm is real symmetric with associated cpu and memory efficiencies. Additionally and importantly, however, neither absorbing potentials nor exterior damping operators are required in the present method, which not only reduces the grid size but also improves the accuracy of the algorithm by removing uncertainties associated with the setting of parameters for these functions. Thus, the method has a number of attractive features which make it potentially superior to existing iterative wave packet methods. The extension to 3D cases is currently under investigation.

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[1] R. Kosloff, Annu. Rev. Phys. Chem. **45**, 145 (1994).
[2] D. J. Kouri, M. Arnold, and D. K. Hoffman, Chem. Phys. Lett. **203**, 166 (1993).
[3] V. A. Mandelshtam, J. Chem. Phys. **108**, 9999 (1998); S. Li, G. Li, and H. Guo, *ibid.* **115**, 9637 (2001).
[4] D. Reignier and S. C. Smith, Chem. Phys. Lett. **366**, 390 (2002).
[5] H. Zhang, D. Reignier, and S. C. Smith, J. Theor. Comput. Chem. (to be published).
[6] J. K. Cullum and R. A. Willoughby, *Lanczos algorithms for large symmetric eigenvalue computations* (Birkhauser, Boston, 1985).
[7] N. Moiseyev, P. R. Certain, and F. Weinhold, Mol. Phys. **36**, 1613 (1978).
[8] V. A. Mandelshtam and H. S. Taylor, J. Chem. Phys. **103**, 2903 (1995); S. K. Gray and G. G. Balint-Kurti, J. Chem. Phys. **108**, 950 (1998); R. Chen and H. Guo, *ibid.* **105**, 3569 (1996).
[9] H. W. Jang and J. C. Light, J. Chem. Phys. **102**, 3262 (1995).
[10] C. Lanczos, J. Res. Natl. Bur. Stand. **45**, 255 (1950).
[11] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes* (Cambridge University Press, Cambridge, 1992).
[12] H. Zhang and S. C. Smith, Phys. Chem. Chem. Phys. **3**, 2282 (2001); H. Zhang and S. C. Smith, J. Chem. Phys. **115**, 5751 (2001).
[13] D. G. Truhlar and C. J. Horowitz, J. Chem. Phys. **71**, 1514 (1979).
[14] S. Li, G. Li, and H. Guo, J. Chem. Phys. **115**, 9637 (2001); H. W. Jang and J. C. Light, Chem. Phys. Lett. **242**, 62 (1995).